Role of Iron Catalyst on Hydroconversion of Aromatic Hydrocarbons

Eisuke Ogata, Xain-Yong Wei[a], Akio Nishijima[b], Tomo Hojo[c] and Kazuyuki Horie
Department of Chemistry and Biotechnology, Graduate School of Engineering,
The University of Tokyo; 7-3-1, Hongo, Bunkyo-ku, Tokyo 113, Japan [A1]

1. Introduction

A symposium on iron-based catalysts for coal liquefaction was held at the 205th ACS National Meeting[1], and some of the papers have been published in *Energy & Fuels*[2]. Reviews of the development of catalysts for coal liquefaction were also published in *Journal of the Japan Institute of Energy*[3], and Ozaki reviewed the results of the studies of upgrading residual oils by means of thermal cracking and coking under reduced pressures, catalytic cracking over nickel ores and iron oxides, and hydrodesulfurization, as well as hydrodemetallization[4]. We reported that catalysis of metallic iron and iron-sulfide catalysts were affected by the S/Fe ratio; the activity increased with pyrrhotite formation and the activity was accelerated by the presence of excess sulfur[5-8]. Activity of pyrite FeS_2 for phenanthrene hydrogenation[9] and activity of natural ground pyrites for coal liquefaction[10] decreased with storage under air. On the other hand, the NEDOL process for a coal liquefaction pilot plant of 150 t/d which is one of the national projects in Japan, will use pyrites as one of the catalysts for the first-stage because FeS_2 has high activity and is low in price. In this paper, we describe in detail the role of iron catalysts in hydroconversion of aromatic hydrocarbons such as diphenyl (DPh), dinaphthyl (DNp) and diarylalkanes (DAAs) constructed with monocyclic aromatic-units and/or bicyclic aromatic-units and both monocyclic and bicyclic aromatic units and linked with from one to three methylene-groups.

2. Experimental

Materials: (1-Naphthyl)phenylmethane (NPM) and di(1-naphthyl)methane (DNM) were synthesized by heating naphthalene (NpH) with benzyl chloride and 1-chloromethylnaphthalene in the presence of metallic zinc powder catalyst, respectively[11], and 1,2-di(1-naphthyl)ethane (DNE) was synthesized by the reaction of 1-bromomethylnaphthalene with metallic iron powder catalyst in boiling water [12]. 1,3-Di(1-naphthyl)propane (DNP) was synthesized by a coupling reaction of 1-naphthylmagnesium bromide with 1,3-dibromopropane in the presence of copper(I) bromide catalyst in hexamethylphosphric triamide (HMPA) solvent [13]. These diarylalkane (DAAs) were purified using conventional methods such as vacuum distillation, separation with silica and alumina column chromatography and recrystallization from the solutions. The other substrates such as 1-methylnaphthalene (1-MN), diphenyl (DPh), 1,1'-dinaphthyl (DNp), diphenylmethane (DPM), 1,2-diphenylethane (DPE), 1,3-diphenylpropane (DPP), triphenyl-methane (TPM), 1-[4-(2-phenylethyl)benzyl]naphthalene (PEBN); hydrogen-donors such as tetralin (THN), 9,10-dihydrophenanthrene (DHP) and 9,10-dihydroanthracene (DHA); and the solvent decalin (DHN), were purchased commercially and further purified, if necessary, by conventional methods. *Catalysts:* Pyrite FeS_2 and metallic iron ultra fine powder Fe were synthesized by Asahi Chemical Industry Co. Ltd. and Vacuum Metallurgical Co. Ltd., respectively. *Procedure:* In typical reactions, 1.0 g of 1-MN or PEBN or 7.7 mmol of DAAs, the prescribed amount of FeS_2 or Fe catalysts and 30 ml of DHN, as well as the prescribed amount sulfur (S/Fe ratio = 2.0) if necessary, were placed in 90 ml or 150 ml stainless steel, magnetically stirred autoclaves. After pressurization with 10 MPa of hydrogen, nitrogen or argon, the

[a] Present Address: [a]Department of Coal Preparation and Utilization, China Univewrsity of Mining and Technology, Xuzhou (221008), Jiangsu, China; [b]Surface Characterization Laboratory, National Institute of Materials and Chemical Research, 1-1, Higashi, Tsukuba-shi, Ibaraki 305, Japan; [c]Department of Industrial Chemistry, College of Science and Technology, Nihon University, 1-8, Surugadai, Kanda, Chiyoda-ku, Tokyo 101, Japan.

autoclave was heated to the desired reaction temperature from 300°C to 400°C within 20 min and maintained for 1 hr. It was then immediately cooled in an ice-water bath. *Analyses:* The reaction products were identified by GC-MS (Shimadzu GCMS QP-1000, equipped with a 0.24 mm (I.D.) x 50 m (L.) glass capillary column chemically bonded with OV-1)and quantified by GC (Shimadzu GC-15A, equipped with the same capillary column). *Oxidation of FeS$_2$ Catalyst:* FeS$_2$ was oxidized at room temperature, 80°C, 150°C and 200°C for the desired time under atmospheric air. The bulk structure of iron catalysts oxidized and recovered after the reaction was analyzed by using XRD (Rigaku Denki Model RINT 2400) and XPS (Perkin-Elmer Model PHI 5500). Substrates and the notations are shown in following:
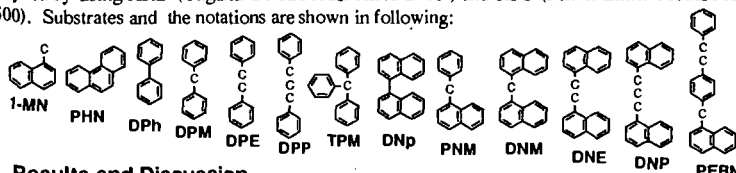
3. Results and Discussion

Thermolysis of aromatic hydrocarbons was strongly affected by the bridged-methylene length, aromatic-ring size in the arylalkane structure, and the presence of molecular hydrogen (H$_2$) in the reaction system as shown in Table 1. Under treaction conditions of 400°C for 1 hr, DPM was very stable in both the absence and presence of H$_2$. The reactivity of diarylalkanes (DAAs) constituted of two phenyl-rings increased in the following order: DPM << DPE << DPP. These conversions were slightly increased by the presence of H$_2$. Generally, the reactivities of DAAs constituted of two naphthyl-rings were higher than those of diphenylalkanes (DPAs). It is particularly remarkable that many radical-adducts between species formed from C$_{alk}$-C$_{alk}$ bond cleavage and solvent DHN molecule was recovered, and many phenylethyldecalins and naphthylethyldecalins were produced especially in the case of diarylpropane thermolyses and the formation was slightly depressed by the presence of gas phase H$_2$ molecule. From other experiments it was shown that the reaction between styrene and DHN under the same reaction conditions formed many phenylethyldecalins as solvent adducts, suggesting that these solvent adducts were produced when arylethylenes were formed in the reaction system. These results ultimately indicate that C-C bond scission was proceeded by a radical chain reaction and the reactivity of DAAs was governed by dissociation energy of C$_{alk}$-C$_{alk}$ and C$_{alk}$-C$_{ar}$ bonds in the absence of catalyst.

Tables 2 and 3 show the effect of bridged methylene length in the diarylalkane structure on the hydroconversion with pyrite FeS$_2$ catalyst at 300°C for 1 hr, and the effect of aromatic ring-size and number in the arylalkane structure. DPE and DPP were not converted even after 10 hrs. The reaction of DPh yielded only cyclohexylbenzene via the hydrogenation of one benzene-ring. DPM hydrocracking also proceeded via the C$_{ar}$-C$_{alk}$ bond scission, but DPM was much less reactive than triphenylmethane (TPM). DNp hydrocracking resulted in the corresponding tetra-hydrogenated 1,1'-dinaphthyls as main products. Reactivity of DNM was the highest in this hydroconversion series. DNM hydrocracking mainly produced naphthalene (NpH) and 1-MN, via hydrogen addition to the ipso-carbon of DNM. Only a small amount of hydrogenated di(1-naphthyl)methanes (H-DNMs) was produced. DNM hydrocracking was much easier than that of DPM and TPM. Drastically different from DNM, the reactions of DNE and DNP mainly yielded the hydrogenated 1,2-di(1-naphthyl)ethanes (H-DNEs) and the hydrogenated 1,3-di(1-naphthyl)propanes (H-DNPs) rather than decomposed products, respectively. The result shows that the cleavage of the C$_{ar}$-C$_{alk}$ linkage in DNE and DNP is much more difficult than that in DNM. The total selectivity of decomposed products in the case of DNp was higher than that in DNE hydroconversion. Reaction of DNP mainly produced hydrogenated 1,3-di(1-naphthyl)-propanes (H-DNPs), and a small amount of hydrocracked products such as NpH and (1-naphthyl)

propane (1-NP). Table 4 shows the effects of Fe and FeS_2 catalysts and reaction temperature on the hydroconversion of DPM. FeS_2 catalyst has more hydrocracking sites than hydrogenation sites, while Fe catalyst has highly active sites and mainly produced hydrogenated diphenylmethanes (H-DPMs).

Table 5 shows the additive effects of hydrogen-donors (H-donors) on DPP thermolysis and the additive effects of metallic Fe and FeS_2 catalysts on DPP hydroconversion at 400°C for 1 hr. DPP conversion decreased with H-donor addition in the order: none > THN >> DHP > DHA. These results are easily understood because the resulting $PhCH_2^{\cdot}$ abstracts hydrogen atoms from the H-donors readily more than it does from DPP. In other words, the H-donors inhibited the radical chain reaction in DPP thermolysis by donating their benzylic hydrogen to $PhCH_2^{\cdot}$. Table 5 also demonstrates the catalytic effects of FeS_2 and Fe on the DPP thermolysis when compared with the non-catalytic reaction of DPP under H_2 of 10 MPa at 400°C. FeS_2 greatly promoted C_{alk}-C_{alk} bond scission as DPP hydrocracking. Under H_2, the rate for DPP hydrocracking in the presence of FeS_2 was ca. 2-fold faster than that in the absence of the catalyst and dramatically decreased the formation of solvent adducts. Fe catalyst promoted DPP hydrogenation, but DPP conversion was low, about the same as that under N_2. This result suggests that Fe catalyst promoted DPP hydrogenation and inhibited thermolysis. The inhibiting effect of Fe on DPP thermolysis remains to be investigated. It appears remarkably that the formation of solvent adducts such as phenylethyldecalins (PEDs) was drastically inhibited by FeS_2 and metallic Fe catalysts.

FeS_2 was oxidized to ferrous sulfate $FeSO_4 \cdot H_2O$ even at room temperature under atmospheric air, and the catalytic activities of oxidized FeS_2 on 1-MN hydrogenation were decreased with increases in the storage time. Recently, Linehan and co-workers [14,15] reported the C-C bond scission activity of PEBN on well-characterized eleven synthesized iron-oxygen compound catalysts in the presence of elemental sulfur and a hydrogen-donating solvent in detail. As shown in Figs. 1 and 2, thermolysis of PEBN under Ar was stable, but the conversion of PEBN was effectively accelerated in the presence of 10 MPa H_2 and the main reaction was changed from C_{alk}-C_{alk} bond scission (*Route [A]*) to C_{ar}-C_{alk} bond scission (*Route [C]*). Metallic Fe catalyst mainly accelerated the hydrogenation (*Route [B]*), and FeS_2 catalyst promoted C-C bond scission of *Route [C]*. FeS_2 catalyst activity was decreased with the oxidation of FeS_2 by oxygen in the air. However, the deactivated FeS_2 catalysts were reactivated by the presence of excess elemental sulfur in the system, and the reaction proceeded along *Route [C]*.

4. Concluding Remarks

Hydroconversion of aromatics and arylalkanes as a model reaction of coal liquefaction and heavy petroleum residue degradation was carried out in the absence or presence of metallic iron Fe and pyrite FeS_2. Thermolysis of some diarylalkanes proceeded slowly by the radical chain reaction. The reaction rate was reduced by the addition of hydrogen-donating solvents and was slightly accelerated in the presence of hydrogen molecules. Metallic Fe catalyst accelerated the hydrogenation of aromatic-rings, especially bicyclic-rings, more than that of monocyclic-rings. FeS_2 catalysts, which is converted to pyrrhotite $Fe_{1-x}S$ under reaction conditions, promoted C_{ar}-C_{alk} bond cleavage of diarylmethanes only, and also promoted the hydrogenation of diarylethanes and diarylpropanes. C-C bond cleavage of arylalkanes was related to the hydrogen-accepting ability, C-C bond dissociation energy and resonance energy of the species after C-C bond scission. Oxidation of pyrites and its catalysis were also investigated. It was found that the catalytic activity of pyrites in the hydrogenation of 1-methylnaphthalene and 1-[4(2-phenylethyl)benzyl]naphthalene decreased with oxidation under air, and deactivated pyrites was reactivated by addition of sulfur to the reaction system.

Acknowledgment

References

1. Preprt."Symposium on Iron-Based Catalysts for Coal Liquefaction", Div. Fuel Chem., 205th ACS National Meeting (Denver), Vol. 38 (No.1),pp-1-238 (1993).
2. Energy & Fuels, 8,(1), (Special issue), p-2-123 (1994).
3. J. Jpn Instit. Energy, 73, (1), (Special issue), p-2-49 (1994).
4. H. Ozaki, Sekiyu Gakkaishi, 36, (3), 169 (1993).
5. E. Ogata, E. Niki, Proc. 27th Conf. Coal Sci. Jpn. Soc. Fuel (Tokyo), pp-115 (1990).
6. X.-Y. Wei, E. Ogata, E. Niki, Chem. Lett., 2199 (1991).
7. X.-Y. Wei, E. Ogata, Z.-M. Zong, E. Niki, Energy & Fuels, 6, 868 (1992).
8. E. Ogata, K. Ishiwata, X.-M. Wei, E. Niki, Proc. 7th Inter. Conf. Coal Sci.(Banff), Vol. II, pp-349 (1993).
9. E. Ogata, T. Suzuki, K. Kawamura, Y. Kamiya, 26th Conf. Coal Sci. Jpn. Soc. Fuel (Sapporo), pp-121 (1989).
10. K. Hirano, T. Hayashi, K. Hayakawa, 30th Conf. Coal Sci. Jpn. Soc. Fuel (Tokyo), pp-161 (1993).
11. S. Futamura, S. Koyanagi, Y. Kamiya, Fuel, 63, 1660 (1984).
12. N. P. Buu-Hoi and N. Hoan, J. Org. Chem., 14, 1023 (1949).
13. J. Nishijima, N. Yamada, Y. Horiuchi, E. Ueda, A. Ohbayashi, and A. Oku, Bull. Chem. Soc. Jpn., 59, 2035 (1986).
14. J. C. Linehan, D. W. Matson, and J. G. Darab, Energy & Fuels, 8, 56 (1994).
15. D. W. Matson, J. C. Linehan, J. G. Darab, and M. F. Buehler, Energy & Fuels, 8, 10 (1994).

Table 1   Effect of Chain-length and Ring-size in the Diarylalkane Structure and 10 MPa of Hydrogen on the Thermolysis at 400°C for 1 hr.

Substrate	DPM		DPE		DPP		DNM	DNE		DNP
Gas Phase	N_2	H_2	N_2	H_2	N_2	H_2	H_2	N_2	H_2	N_2
Conv.(%)	0	0	2.3	3.6	39.9	46.5	2.1	45.8	73.0	35.6
Selectivity (mol %)										
Benzene	0	0	0	98.2	0	3.4	0	0	0	0
Naphthalene	0	0	0	0	0	0	61.7	1.5	12.6	0
Arylmethane	0	0	200[a]	101.8[a]	100[a]	96.6[a]	61.7[b]	174.4[b]	132.2[b]	105.0[b]
Arylethane	0	0	0	98.2[c]	2.9[c]	16.5[c]	0	1.4[d]	9.7[d]	6.4[d]
Arylethylene	0	0	0	0	9.8[e]	6.2[e]	0	0	0	14.9[f]
Arylpropane	0	0	0	0	0	3.4[g]	0	0	0	0
Arylalkyldecalins	0	0	0	0	87.4[h]	73.4[h]	38.3	4.7	14.9	73.7[i]

a: Toluene; b: Methylnaphthalene; c: Ethylbenzene; d: Ethylnaphthalene; e: Styrene; f: Vinylnaphthalene; g: Propylbenzene; h: Phenylethyldecalins; i: Naphthylethyldecalins.

Table 2   Effects of Chain-length in the Diarylalkane Structure on Hydroconversion with Pyrite FeS2 Catalyst at 300°C for 1 hr.

Substrate	DPh	DPM	DPE	DPP	DNp	DNM	DNE	DNP
Conv.(%)	0.5	3.1	0	0	11.4	91.7	50.7	51.1
(10 hrs.)[a]	(6.2)	(36.1)	(0)	(0)	---	---	---	---
Selectivity(mol %)								
Benzene	0	100	0	0	0	0	0	0
Naphthalene	0	0	0	0	17.3	95.7	1.8	10.3
Arylmethane	0	100[b]	0	0	0	89.0[c]	2.3[c]	tr[c]
Arylethane	0	0	0	0	0	0	0.4[d]	tr[d]
Arylpropane	0	0	0	0	0	0	0	7.0
H-DAAs[e]	100[f]	0	0	0	43.3[g]	2.9	86.8	88.1

a: Reaction Time 10 hrs; b: Toluene; c: 1-Methylnaphthalene; d: Ethylnaphthalene; e: Hydrogenated Diarylalkanes; f: Cyclohexylbenzene; g: Hydrogenated Dinaphthyls.

Table 3 Effects of Ring-size and Number in the Diarylmethane Structure on Hydrogenation with Pyrite FeS₂ Catalyst at 300°C for 1 hr.

Substrate	DPM	TPM	NPM	DNM
Conversion (%)	3.1	36.1[a]	21.4	86	92
Selectivity (mol %)					
Benzene	100	99	102.6	tr	0
Naphthalene	0	0	0	64	96
Arylmethane	100[b]	99[b]	2.6[b]	71[b]	89[c]
Diarylmethane	---	---	97.4[d]	12[e]	---
Tetralins	0	0	0	9.3	7.9
H-DAAs[f]	0	1.5	tr	15	2.9

a: Reaction Time 10 hrs; b: Toluene; c: 1-Methylnaphthalene; d: Diphenylmethane; e: (2-Naphthyl)-phenylmethane; f: Hydrogenated diarylalkanes.

Table 4 Effects of Iron Catalysts and Reaction Temperature on Hydroconversion of Diphenylmethane for 1 hr.

Temp. (°C)	Catalyst (g)	Conv. (%)	Selectivity (mol %)					
			CHx[a]	PhH[b]	MCH[c]	Tol[d]	DCHM[e]	BCH[f]
300	Fe (0.23)	58.4	0	0	0	0	13.4	86.6
300	FeS₂ (0.50)[g]	3.1	0	100	0	100	0	0
400	Fe (0.02)	79.3	3.2	0	9.8	0	42.1	57
400	FeS₂ (0.50)[g]	59.1	0	98	0	97.2	2.4	0

a: Cyclohexane; b: Benzene; c: Methylcyclohexane; d: Toluene; e: Dicyclohexylmethane; f: Benzylcyclohexane; g: Addition of Sulfur 0.05 g.

Table 5 Additive Effect of Hydrogen-Donating Solvents and Iron Catalysts on Conversion Reaction of Diphenylpropane at 400°C for 1 hr.

Additive (g)	Gas Phase	React. Time(hr)	Conv. (%)	Selectivity (mol %)						
				PhH[b]	Tol[c]	EiPh[d]	Styr[e]	CHPP[f]	BCHP[g]	PEDs[h]
None	0	N₂	1	39.9	0	100	2.9	9.8	0	0	87.4
THN	7.5[i]	N₂	1	28.6	0	100	3.8	19.5	0	0	76.7
DHP	7.5[i]	N₂	1	7.4	0	100	6.4	39.8	0	0	53.8
DHA	7.5[i]	N₂	1	3.8	0	100	60.9	20.8	0	0	0
None	0	H₂	1	46.5	3.4	96.6	16.5	6.2	0	0	73.4
None	0	H₂	2	70.7	5.1	94.9	29.1	2.0	0	0	68.9
Fe	0.02	H₂	1	40.0	6.6	63.4	56.2	0	24.7	5.3	13.8
Fe	0.02	H₂	2	65.9	10.7	53.9	48.8	0	26.9	8.5	15.8
FeS₂	0.50[j]	H₂	1	69.7	8.7	87.6	87.2	2.6	3.7	0	0
FeS₂	0.50[j]	H₂	2	86.2	9.9	86.8	86.5	1.9	3.3	0	0

a: Reaction Condition DPP 7.5 mmol, DHN 30 ml, PH2 10 MPa; b: Benzene; c: Toluene; d: Ethylbenzene; e: Styrene; f: Cyclohexylphenylpropane; g: Bicyclohexylpropane; h: Phenylethyldecalins; i: mmol; j: Addition of Sulfur 0.05 g.

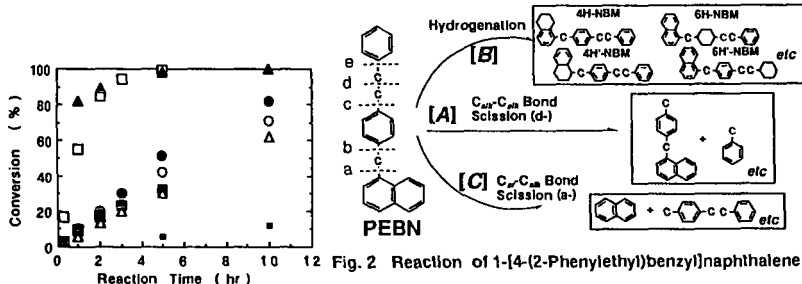Fig. 2 Reaction of 1-[4-(2-Phenylethyl)benzyl]naphthalene

Fig. 1 Effect of Reaction Time on the Conversion Reaction of 1-[4-(2-Phenylethyl)benzyl]naphthalene.

Reaction Conditions: PEBN 1.0 g, DHN 30 ml, PH₂ 10 MPa,
O : H₂ - 350°C, ● : H₂ - 380°C, □ : H₂ - 400°C, ■ : Ar - 380°C,
■ : Ar - 400°C, △ : H₂ - 380°C - DHA Addition(DHA/PEBN = 3.0),
▲ : H₂ - 380°C - Fe Cat.(0.05 g).